

[Contribution from the John Harrison Laboratory of Chemistry.]

OBSERVATIONS ON COLUMBIUM AND TANTALUM.

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In 1801 Hatchett, while studying minerals in the British Museum came upon a specimen from Haddam, Conn., which attracted his attention because of its rather high specific gravity and its brilliant black color. A portion of this material was given him for examination, with the result that he discovered in it a new metallic acid, to the metal of which he applied the name columbium. It was his earnest hope that he might obtain larger quantities of the American mineral in order to exhaustively study the new element, and it is of interest to remark that Hatchett fondly expected this material assistance from Thomas Peters Smith, a member of this Society and an enthusiast in chemical science, who on his return from England met an untimely death on shipboard.

In 1802 Ekeberg, of Sweden, while examining an unknown mineral, found that it contained a new metallic acid, to the metal of which acid he assigned the name tantalum, because "when placed in the midst of acids it is incapable of taking any of them up and saturating itself with them." Later, Wollaston (1809) strove to prove that columbium and tantalum were identical. In this he failed. The few reactions known even at that early day differentiated the new elements. About 1840, Heinrich Rose, in studying similar minerals, from other localities, came to the conclusion that the American mineral contained an element absolutely different from tantalum, and called it niobium. Subsequently, owing to his inability to account for the peculiar products which he got by chlorinating a mixture of the oxide of the new element and carbon, he asserted that, in addition to niobium, there was present pelopium (1846). Later (1853), however, he seems to have arrived at the opinion that niobic acid and pelopic acid were different oxides of niobium. The first he called niobic acid and the second hyponiobic acid. Hermann, also, contributed to the uncertainty which surrounded the two elements (columbium of Hat-

chett and tantalum of Ekeberg) in that he announced the existence of ilmenium; but it was not generally accepted by chemists. Hermann, however, persisted in his declaration that it occurred along with the other two elements to which reference has been made. v. Kobell believed that he had detected dianium in allied minerals. This unfortunate state of affairs prevailed until the early sixties, when Marignac, after a careful study of a number of minerals from various localities, announced the existence in them of but two elements—the columbium of Hatchett and the tantalum of Ekeberg—and added that the confusing reactions which had perhaps led Heinrich Rose—but most certainly, Hermann and von Kobell—astray were to be explained by the presence of titanium in all tantalites and columbites. It is only fair to say that Marignac never succeeded in obtaining titanium from any one of the minerals in which, according to him, it occurred, associated together with columbium and tantalum. Indeed, in his concluding paper on columbium he frankly acknowledged that the columbium compounds, which he used for the determination of the atomic weight of the metal, contained titanium, and that he knew of no method by which the latter could be separated from columbium. Marignac's conclusion was accepted by the chemists of the world as final.

When we come to examine the evidence which Marignac gives for the presence of titanium, we find that it is, practically: that the recrystallization of a double fluoride of columbium and potassium, supposed to contain titanium, gave rise, gradually, to a fraction which became more insoluble in water and the molecular weight of its acid oxide approached, within ten or more units, that required by titanous oxide. It is well to bear in mind that at no time did Marignac, whose ability and keen insight one would not for a moment question, give any tests which are ordinarily regarded as indicating titanium. He assumed it to be present on the evidence mentioned above, viz: the greater insolubility of the double fluoride and an approximate molecular weight corresponding to that required by titanous oxide. Ever since Marignac's day chemists the world over have tacitly accepted titanium as associated with columbium in columbites. They have also estimated its quantity by methods suggested from time to time. One of these methods is based on the color reaction which titanium salts give with hydrogen peroxide. Its intensity, compared with that shown

by a known amount of titanium, has been regarded by most analysts as entirely satisfactory. For the determination of the amount of titanium in columbium many methods have been proposed, but this is not the place to discuss them or their value.

As late as 1877, in the last paper published by Hermann, he announced the element neptunium and claimed to have obtained it from the acid mother liquors remaining after tantalum potassium fluoride, ilmenium potassium fluoride and columbium potassium fluoride had been crystallized out. The particular mineral in which he observed it was a columbite from Haddam, Conn.; in other words, the same mineral in which columbium had been originally discovered by Hatchett.

The existence of neptunium has never been contradicted. This is probably because the majority of chemists thought that the verdict in regard to the constitution of tantalites and columbites had been given by Marignac, and that the numerous, unusual reactions of the metallic acids contained in those minerals, noted and commented upon at various times by Heinrich Rose, von Kobell, Blomstrand and Hermann, were all due to the contaminating influence of titanium.

The two elements, columbium and tantalum, in their derivatives, have received comparatively little attention within the last quarter of a century, although at intervals attempts have been made to clear up the mystery which, in a certain sense, surrounds them. In this laboratory, several investigations upon derivatives of them have been made. These being not wholly satisfactory, about three years ago, 50 lbs. of columbite from South Dakota and 25 lbs. from Haddam, Conn., were worked up, with a view of getting an abundant supply of starting-out material; with the view, also, of studying anew the various derivatives of both columbium and tantalum. In the year 1903-1904, Dr. R. D. Hall devoted, in this laboratory, much time and labor to the double fluorides of tantalum and columbium. He made a comparative study of the reactions of the same with the reactions of titanium. His results have been published, but from an examination of them it will be observed that he was not able to find any tests, while using the double fluorides, which differentiated titanium from columbium so thoroughly that he could expect to obtain a complete separation of these two most interesting elements. It is true that he was able, by precipi-

tating potassium columbium fluoride incompletely with ammonia, to get a columbium oxide, which apparently gave no response to the hydrogen peroxide test upon its application, or to the reagent called chromotropic acid. Hence he inferred that he had eliminated the titanium from the columbium. More recent work with large quantities of material has demonstrated that in the latter cases it was impossible to entirely remove the metallic acid which gave the color tests. It was further found that by the action of sulphur monochloride upon the oxides of columbium and titanium, corresponding chlorides were produced; but again, it proved impossible to wholly expel the titanium from the columbium by this process, notwithstanding titanium chloride is an exceedingly volatile liquid and columbium chloride a solid, crystalline body.

In the present year, we have, in this laboratory, prepared large quantities of the double fluoride of tantalum and potassium, and found no difficulty whatsoever in eliminating from it every trace of what was supposed to be the titanium double fluoride.

Having thus, at our disposal, such generous amounts of pure tantalic oxide, free from columbic oxide, in short, really pure tantalic oxide, it was determined to make a new study of the double fluorides of tantalum with the alkali metals and organic bases. This was undertaken in order to discover, if possible, why Dr. Pennington, when working in this laboratory in 1895, obtained double fluorides of tantalum and columbium with cæsium, which showed these unusual formulas: $15\text{CsF} \cdot \text{TaF}_5$ and $7\text{CsF} \cdot \text{CbF}_5$, which varied so widely from those generally followed by the double fluorides of tantalum and columbium, and were not in accord with the law proposed for double halides (*Amer. Chem. Jour.*, v. 291).

At the outstart it was thought that this re-investigation of the double fluorides would prove to be an easy and simple matter. But it was not long until it was seen that the discordant results of Dr. Pennington were probably due to the fact that there was more than one cæsium tantalum fluoride. Indeed, the latest work done in this laboratory, by Mr. C. W. Balke, proves that there are two cæsium tantalum fluorides, two rubidium tantalum fluorides, two sodium tantalum fluorides, two ammonium tantalum fluorides, and so forth, of these ratios:

TaF ₅ .CsF	2TaF ₅ .3RbF
TaF ₅ .2CsF	TaF ₅ .2NaF
TaF ₅ .2NH ₄ F	TaF ₅ .3NaF
TaF ₅ .3NH ₄ F	TaF ₅ .2KF

The existence of several such double fluorides with each of the alkali metals naturally raises the question whether these salts ought to be used for the determination of the atomic weight of tantalum, inasmuch as each salt is likely to be contaminated with smaller or larger quantities of the other, depending upon the condition or the care with which they are prepared. Marignac used potassium tantalum fluoride and ammonium tantalum fluoride in his re-determination of the atomic weight of tantalum. It would seem, from the study of the salts just mentioned, that even this skilled and careful analyst could not have been sure that he had a definite, homogeneous body in the determinations which he made. Of course, if there was even a slight amount of a second salt in the salt used for the atomic weight work, it would naturally vitiate the final result. Of all the double fluorides of the alkali metals and bases with tantalum which have thus far been studied by Mr. Balke, that of sodium and tantalum, of the ratio 3 to 2, seems to be the one having some definite and most stable characteristics. We hope to re-determine the atomic weight of tantalum, but it is not probable that we shall use any one of the double fluorides, of which mention has been made, although they appeal strongly because of the ease with which they can be crystallized. The uncertainty, however, as to whether they are really absolutely of one definite ratio every time that they are crystallized is uncertain. Hence they had better be abandoned in atomic weight determinations.

The question may also be asked, may not the double fluorides of columbium with the alkali metals, which have been used for atomic weight purposes, been contaminated with salts of varying ratios? This point will receive attention.

Turning again to columbium, it seems proper to record that having eliminated the tantalum completely from a mixture of oxides obtained from Haddam columbite, the remaining potassium columbium oxy-fluoride was crystallized a number of times from water and also from solutions containing much hydrofluoric acid. This procedure finally gave a mother liquor that was decidedly acid. A metallic acid remained in this mother liquor. According to Her-

mann, in his communication of 1877, this acid should be neptunic acid. Therefore, the acid mother liquor was treated as directed by Hermann; namely, it was evaporated, the residue was dissolved in water and the boiling solution precipitated with an excess of caustic soda. The precipitate, after the liquid had become cold, was filtered out, pressed thoroughly from adherent water and then boiled with 25 times its own weight of pure water. Everything dissolved. The solution was perfectly clear. On cooling, there separated from it the beautiful needle-like crystals of sodium columbate. According to Hermann, the precipitate which was collected, pressed out and then boiled with water, should, if neptunium were present, have left a slimy mass, insoluble in water. This, Hermann said, was sodium neptunate. It should be observed that our experiments were made with the final acid liquors obtained from the double fluorides present in columbite from Haddam; further, that we proceeded in strict accordance with the directions of Hermann and having done all this, did not obtain a gelatinous mass which might have been sodium neptunate. In Hermann's communication, to which reference has been made so frequently, he lays great stress on the fact that the distinguishing reaction of neptunium is the beautiful golden yellow color which sodium neptunate imparts to a salt of phosphorus bead in the *reducing flame*. It is needless to add that we tried on different occasions to find neptunium, according to the directions of Hermann; but our search was fruitless. On one occasion, however, we obtained a mass, not great in amount, which, in the inner blow-pipe flame, did impart a yellow color to the salt of phosphorus bead, but more careful examination of this residue demonstrated that it contained tantalum, iron and some columbium. The intense golden yellow color, which was so strongly emphasized by Herman, we could not get; so that it is very probable that neptunium, like ilmenium and the other metals announced from time to time as present with columbium and tantalum must really be placed in the list of defunct elements. It has not been our wish to bury this candidate for elemental honors. Indeed, we would have been only too glad to have found the evidences of its existence and to have confirmed the observation of that earnest and sincere student of chemical science, who, in his tireless labors, frequently felt confident that he had fallen upon the cause of the varying results observed with columbium and tantalum.

In this connection it may be added that, having freed the tantalum and columbium oxides as thoroughly as possible from ordinary contaminations, the problem of removing tungsten and tin confronted us. After much experimentation, we found that the certainty of the removal of these impurities could only be had by fusing the tantalum and columbium oxides with sodium carbonate and sulphur. It is true that small quantities of tantalum and columbium will be lost, being carried along with the tungsten and tin, but as we were seeking a method of purification and not a separation, we adopted this course. It is the one which was pursued by Heinrich Rose. Our own experience leads us to say that the removal of tungsten and tin from columbium and tantalum oxides cannot be realized by digestion with ammonium sulphide. Indeed, not only did we find the fusion with the sodium carbonate and sulphur necessary, but that working in large quantities of material, as in our case, two and three refusions with these reagents were found necessary. Another point of interest in connection with the purification of the tantalum and columbium oxides may be mentioned. It has frequently been said that in crystallizing out the double fluorides of these metals, if titanium be present with them, it will be found in the potassium tantalum fluoride. We have encountered no difficulty in getting potassium tantalum fluoride perfectly free from what is supposed to be titanium by one or two crystallizations. It has been assumed that as potassium titanium fluoride is rather insoluble in water, it would naturally go with potassium tantalum fluoride. This, however, seems to be an incorrect observation. It masses with the columbium potassium fluoride; at least the element which gives the yellow color with hydrogen peroxide, or a rose red with chromotropic acid is always found associated with the columbium. How to free the columbium from titanous acid we do not know. We are in precisely the same position as that of Marignac, notwithstanding we have probably made greater efforts than he to remove it from the columbium. It is this point in our investigation upon which we have been continuously at work for the last year. We have tried fractional precipitation with ammonia water, fractional crystallization of the double fluorides, fractional chlorination of the oxides in the presence of carbon and the action of numerous organic bases, without finding any way of effecting a separation. Indeed, the separation of columbium and titanium is a problem

which the analyst has not solved up to the present. As remarked, it has received and is receiving our daily attention. Once having achieved this result and having definitely determined the character of the color-giving metallic acid, or proved it to be titanium, without any further doubt, we then hope to subject the purified columbic oxide to a searching review in all its derivatives, just as we are now doing with the compounds of tantalum. In anticipation, it may be said that there are some most interesting complexes of tungstic acid with tantalic oxide and also of tungstic acid and columbic acid. These are under study at present. These complexes, also, have brought analytical problems that are most puzzling. Yet our progress with them leads us to hope for a separation and a satisfactory solution of the same.

Some attention has likewise been given to per-tantalates and per-columbates. It would not be the least surprising to find these derivatives answering admirably for atomic weight work.

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